Element mapping in ilmenite ores with focus on phosphorus

Rikke Weibel

GEOLOGICAL SURVEY OF DENMARK AND GREENLAND MINISTRY OF THE ENVIRONMENT



Element mapping in ilmenite ores with focus on phosphorus

Rikke Weibel

Released 01.11.2012



GEOLOGICAL SURVEY OF DENMARK AND GREENLAND MINISTRY OF THE ENVIRONMENT

Abstract

Computer controlled scanning electron microscopy (CCSEM) is a powerful tool to examine the element geochemistry of ilmenite ores on a grain by grain basis. The methodology is capable of mapping the distribution of up to 18 elements (Si, Al, Ti, Fe, Mg, Mn, Na, K, Ca, P, S, Cr, Ni, Cu, Zr, Nb, Y, Ce) but the principal focus in this report is on phosphorus, owing to its role in blinding filters at the DuPont DeLisle pigment manufacturing plant. The element mapping and quantitative analyses by the microprobe have been performed on selected ore samples. The results have been compiled together with previous investigations such as bulk XRF, CCSEM and ICP-MS on the same and other samples.

Element mapping by microprobe of ilmenite grains in selected ore samples demonstrates that P_2O_5 is located in the altered parts of the ilmenite grains, where the TiO_2 content is highest. There seems to be no correlation between the phosphorus content in the detrital ilmenite and the phosphorus content in its alteration product. Phosphorus inclusions seem to be of minor importance. Consequently, the phosphorus must be incorporated into the ilmenite grains during the alteration process. The alteration of ilmenite takes place through two steps: pseudorutile and leucoxene. Pseudorutile forms by iron diffusion through the ilmenite lattice and oxidation of the remaining iron. Leucoxene forms by a complete rearrangement of the crystal structure and presumably takes place by an incongruent dissolution process followed by epitactic precipitation of titanium oxide crystals in a porous network.

Microprobe analyses of selected ore samples show an increase in phosphorus content with increasing TiO_2 , Al_2O_3 and partly CaO and SiO_2 . Similar observations can be done from the element maps. These associations suggest that phosphorus is located in minute alumino-phosphate minerals or alumino-phosphate-sulphate minerals, which probably formed inside the porous leucoxene network of the altered parts of ilmenite.

Comparison of microprobe analyses of P_2O_5 in altered ilmenite with CCSEM investigation of P_2O_5 in ilmenite and leucoxene show that CCSEM results are highly reliable, as they are based on a large number of grains. Computed bulk ore phosphorus content (from CCSEM) is less reliable, as it is influenced by statistically relatively rare phosphorus grains (for example xenotime and monazite). Therefore evaluation of the ore should be based on the P_2O_5 content in ilmenite and leucoxene. Consequently the following evaluation of ores is suggested:

XRF bulk rock: $P_2O_5 < 0.1 \%$	NO PROBLEMS EXPECTED
XRF bulk rock: $P_2O_5 > 0.1$ %	CCSEM DETAILED TEST REQUIRED
CCSEM ilmenite + leucoxene: $P_2O_5 < 0.1$ %	ON BASIS OF TI-MINERAL COMPOSITION
	NO PROBLEMS EXPECTED

CCSEM ilmenite + leucoxene: P₂O₅ = 0.1 % BORDERLINE

CCSEM ilmenite + leucoxene: P₂O₅ > 0.1 % PROBLEMATIC RESPONSE EXPECTED

CCSEM of all investigated samples from Denmark, India and Madagascar all show increased phosphorus content with increasing titanium content, i.e. with increasing degree of alteration. The investigated bed rock samples from India contain the least altered ilmenite with the lowest P_2O_5 content. Depositional environments characterised by relatively young deposits in tropical climate or glacial deposition in arctic and later temperate climate result in ilmenite with low degrees of alteration and low incorporation of phosphorus. The shallow marine Miocene Danish deposits show a remarkably lower degree of alteration and lower phosphorus content than the contemporaneous shoreface deposits with wash-over fans on barrier islands. This indicates that, besides the source material, the depositional environment and the climatic conditions and therefore the possibility of leaching influence the degree of ilmenite alteration.

Content

	7
Methodology	8
Samples	9
Results	10
Element maps	10
Quantitative analyses	16
CCSEM	22
P ₂ O ₅ in ilmenite in relation to depositional environment	26
India	26
Denmark	26
Madagascar	
Discussion	31
	31
Location of phosphorus in ilmenite	
Location of phosphorus in ilmenite Alteration of ilmenite	
Location of phosphorus in ilmenite Alteration of ilmenite Depositional environment influence on the P ₂ O ₅ content	
Location of phosphorus in ilmenite Alteration of ilmenite Depositional environment influence on the P ₂ O ₅ content Evaluation of ore quality	
Location of phosphorus in ilmenite Alteration of ilmenite Depositional environment influence on the P ₂ O ₅ content Evaluation of ore quality Conclusion	
Location of phosphorus in ilmenite Alteration of ilmenite Depositional environment influence on the P ₂ O ₅ content Evaluation of ore quality Conclusion Recommendations	
Location of phosphorus in ilmenite Alteration of ilmenite Depositional environment influence on the P ₂ O ₅ content Evaluation of ore quality Conclusion Recommendations Acknowledgement	
Location of phosphorus in ilmenite Alteration of ilmenite Depositional environment influence on the P ₂ O ₅ content Evaluation of ore quality Conclusion Recommendations Acknowledgement References	

Appendix I

Purpose

This study has been initiated to reveal features in ilmenite ore that relates to problems during processing. Phosphorus is of major concern because ilmenite ores high in phosphorus (generally $P_2O_5 > 0.10$ wt%) may result in the blinding of filters at the DeLisle deep-well operation. The objective is to utilise CCSEM to characterise element distribution in ilmenite ores with the focus on phosphorus. Previous investigations have shown that mainly phosphorus, located in ilmenite grains, seems to be causing problems (Roger McLimans and Dirk Frei, personal communication, 2006). The phosphorus content seems to be related to the degree of leucoxene alteration in the ilmenite grains. Element mapping by microprobe has been used to support this suggestion.

Methodology

The element mapping and quantitative analyses of the ilmenite grains were performed by electron microprobe analysis on a JEOL© JXA-8200 at an acceleration voltage of 15kV and a beam current of 15nA. Carbon-coated polished blocks of the ilmenite ores were applied for these tests. Probe scan was used for element mapping of selected areas of the leucoxene altered ilmenite grains. Approximately 20 ilmenite grains from each sample were analysed. The quantitative analyses of leucoxene result in relatively low totals mainly due to intracranial porosity, and consequently polishing and carbon-coating problems, and to some extent non-analysed elements, such as H_2O (in pseudorutile) and REE. Therefore the quantitative results have been normalised to 100 %.

The element mapping results have been compared with earlier results from CCSEM (computer controlled scanning electron microscope) and XRF (X-ray fluorescence) results.

Samples

Sample	Scott rank	CCSEM	ICP- MS	Element maps	Quantitative analysis
2003302 (East Ten- nessee) 2003303 (Florida)		X X	X X	X X X	X X
2003304 (India) 2003305 (Malaysia)		X X	X X	X X	X X
2003306 (Ukraine) 2003307 (Vietnam)		X X	X X	X X	X X
MALAYSIAN 101303- 35A ILUKA-VIRGINI 10.15.03-91	8 10	x x		X X	
ILUKA-FLA 101503-93 AUSTRA-ILUKA E105202-19	5 ? 8	X X		X X	(X) X
AUSTRA-CSL E105202-2 AUSTRA-TIWES TC- !OX-2001T	8 8	x x			
DORAL 10.22.08-97 VIETNAMESE E98651-105	10 10-5	X X		X X	X X
INDIAN E105202-7 UKRAINIAN 9.22.03- 24	1	X X		X X	X X

 Table 1. Overview of analyses on the different samples.

Scott rank is an empirical evaluation of the quality of ilmenite ores during processing: 10 = very good, 1 = very bad.

Results

Element maps

The analysed elements include Ti, Si, P, Fe, Mn, Mg for all samples. Selected samples have additionally been analysed for Al, K and Ca. The alteration product of ilmenite is pseudorutile, leucoxene or a combination of both. X-ray diffraction (XRD) or optically reflected light investigations have not been performed in order to distinguish precisely between pseudorutile and leucoxene. Therefore the term 'leucoxene' has been applied to all alteration products of ilmenite, though it may actually include some pseudorutile. In this report a chemical definition is applied for ilmenite, leucoxene and rutile; ilmenite: Ti: 42.3 – 66.8 ATOMIC %, leucoxene: Ti: 66.8 – 85.8 ATOMIC % and rutile: Ti: < 85.8 ATOMIC %.

The element mapping of ilmenite grains in selected ore samples shows that P_2O_5 is located in the altered parts of the ilmenite grains where the TiO₂ content is highest (Appendix 1). Phosphorus inclusions (for example monazite or xenotime) seem to be of minor importance. But one has to remember that this is based on element maps covering restricted parts of the grains (though specifically selected where an inclusion appeared) and a limited number of analysed grains (246 in all). A brief description is presented for each investigated sample and summarised in Table 2. Examples of element maps from each of the investigated samples can be found in Appendix 1.

Indian E105202-7

The Indian E105202-7 sample is dominated by intensely altered ilmenite grains, though some internal original ilmenite remnants also occur. The alteration appears with two or more zones of leucoxene. The alteration of ilmenite to leucoxene started around rims, cracks and along crystallographic weakness zones (along the {0001} plane) in the detrital ilmenite. The element maps of the Indian E105202-7 sample show phosphorus concentration typically in the outermost zone of leucoxene (Appendix 1).

2003304 (India)

The 2003304 (India) sample contains several intensely altered grains, but also grains with remnants of original ilmenite. Leucoxene with up to 3 zones have been identified (Fig. 1 and 2). The 2003304 (India) sample has element maps with a simple relation to leucoxene alteration, as observed in other samples, or with a complex distribution of phosphorus, which is linked to certain zones in the zoned leucoxene. The phosphorus may occur in the outermost alteration rim and also in an inner zone as observed in Fig. 1 and Appendix 1.

Ukrainian 9.22.03-24

The Ukrainian 9.22.03-24 sample is characterised by intensely altered ilmenite grains, which only extremely rarely contain remnants of original ilmenite. The element maps generally show a homogeneous phosphorus distribution in the altered grains. The phosphorus

only appears to be present in high amounts in leucoxene when compared with ilmenite remnants and inclusions of different mineralogy (Appendix 1).

2003306 (Ukraine)

The 2003306 (Ukraine) sample is also dominated by intensely altered ilmenite grains and only rarely are remnants of the original ilmenite grain preserved. The element maps of the 2003306 (Ukraine) sample show no or only very weak concentration of phosphorus in leucoxene.

2003302 (East Tennessee)

The 2003302 (East Tennessee) sample is characterised by altered ilmenite grains, commonly containing detrital remnant in the centre of the grains, but some grains are completely altered. The element maps of the 2003302 (East Tennessee) sample show a relatively higher phosphorus concentration in the leucoxene altered parts of the grain than in the detrital ilmenite. The leucoxene altered parts are also characterised by being relatively rich in Si. Occasionally leucoxene alteration occurs in two (or even more) zones, the innermost being P-rich whereas the outermost is P-poor but Fe-rich (Fig.3; Appendix 1). Colloidal leucoxene also occurs with relatively higher concentrations of P than the original ilmenite remnants.

2003303 (Florida)

The 2003303 (Florida) sample is characterised by intensely altered ilmenite grains with rare remnants of the original ilmenite grain. Element maps of the 2003303 (Florida) sample show increased phosphorus concentration in the leucoxene altered parts of ilmenite grains (Fig. 3). The leucoxene alteration commonly penetrates along a honeycomb texture arranged around a centre with former hematite exsolution lamellae, now dissolution voids (Appendix 1).

Vietnamese E98651-105

In the Vietnamese E98651-105 sample the ilmenite grains appear with a wide range of alteration, varying from very intense to only weak alteration along rims. The element maps showed concentration of phosphorus in leucoxene in some of the ilmenite grains, whereas other ilmenite grains contained phosphorus in equal amounts in altered and unaltered parts (Appendix 1). Aluminium always appears in higher concentrations in the leucoxene altered parts, and sometimes in association with phosphorus. Silicon did not occur together with aluminium as observed in other samples.

2003307 (Vietnam)

The 2003307 (Vietnam) sample is dominated by weakly altered ilmenite grains, but some intensely altered grains also occur, which indicates that there might be two different ilmenite sources. It has been confirmed (Stendal 2004) that the supplier of Vietnam ilmenite ore mixes two different ilmenite types in order to gain the necessary high TiO₂ content. The element maps show that phosphorus is evenly distributed in the leucoxene and ilmenite in weakly altered ilmenite grains. Whereas intensely altered ilmenite grains showed increased phosphorus content in the leucoxene compared to the detrital ilmenite (Appendix 1).

Malaysian 101303-35A

The ilmenite grains occur with several degrees of alteration in the Malaysian 101303-35A sample. The element maps show a weakly increased phosphorus content in the leucoxene altered parts of the ilmenite grains (Appendix 1). Phosphorus enriched areas are more clearly identified in the intensely altered grains. Aluminium and silicon also occur in increased amounts in the leucoxene altered parts. As Al and Si show no relation to K, Ca and Mg, these elements are hardly sited in the clay minerals.

2003305 (Malaysia)

The 2003305 (Malaysia) sample is dominated by intensely altered ilmenite grain with some remnants of original ilmenite. The element maps show higher phosphorus concentrations in the leucoxene altered parts than in the detrital ilmenite or the least altered parts of the ilmenite grains.

Austra-Iluka E105202-19

The Austra-Iluka E105202-19 sample is dominated by ilmenite grains weakly altered along rims and cracks, and typically occurs with preserved original ilmenite remnants in the centre of the grain. The element maps show no increased phosphorus content in the altered areas, not even in grains with distinct alteration of ilmenite to leucoxene is the phosphorus content higher in the leucoxene altered parts (Appendix 1).

Iluka-FLA 10.15.03-93

The Iluka-FLA 10.15.03-93 sample is characterised by intensely altered grains with rare remnants of the original ilmenite. The element maps show that phosphorus occurs in slightly higher concentrations in the outermost leucoxene-altered parts of ilmenite grains (Appendix 1). The leucoxene altered parts are characterised by higher titanium and silicon concentrations; whereas iron, manganese and occasionally magnesium occur in highest amounts in the least altered parts.

Iluka Virgini 101503-91

The ilmenite grains occur with varying degrees of alteration, from almost no alteration to intensely altered grains in the Iluka Virgini 101503-91 sample. The element maps generally showed equal phosphorus content in the original and the altered parts of the ilmenite grains (Appendix 1). A few grains, though, showed increased phosphorus contents (besides increased Si, Al and occasionally Ca contents) in the leucoxene altered parts of ilmenite.

Doral 102208-97

The Doral 102208-97 sample contains intensely altered ilmenite grains with some original ilmenite remnants. The element maps showed no increased phosphorus content in the altered areas, despite intensive alteration of ilmenite to leucoxene (Appendix 1). The leucoxene alteration generally also resulted in increased amounts of Al and Si, whereas Fe, Mn and occasionally Mg were concentrated in the original detrital ilmenite grains. Raised Al and Si amounts are not related to increasing K, Ca or Mg contents. Therefore it seems unlikely that alumina and silica should be related to clay minerals.



Figure 1. Several alteration zones, the innermost zone contains P, Ti and Si, the second zone contains Fe, Ti and Mn and the outermost zone contains P, Ti and Si. Sample India (2003304) Map 86 (060606).

Figure 2. Strongly leucoxene altered ilmenite grain which contains small detrital remnants appearing as elongated islands (white in BSC) which reflects the original crystallography of the ilmenite. Phosphorus seems to be concentrated in the darkest grey zone (BSC) inside the altered grain. Sample India (2003304) Map 95 (060606).



Figure 3. Ilmenite grain with detrital ilmenite core surrounded by leucoxene alteration zones, innermost zone is Ti-Si rich, second zone is Fe-rich, and outermost zone contains P, Ti and Si. Sample East Tennessee (2003302) Map 15 (060606).

Figure 4. *Phosphorus is concentrated in the leucoxene alteration, which penetrated along cracks in the ilmenite grain. Sample Florida (2003303) Map 47 (060606).*

Somple	Scott	XRF	Element mono
Sample	rank	$P_2O_5(\%)$	Element maps
INDIAN E105202-7	1	0.15	Intensely altered ilmenite with some original ilmenite remnants. P is concentrated in the outermost zone of leucoxene.
UKRAINIAN 92203-24	1	0.12	Intensely altered ilmenite. P is concentrated in the outermost zone of leucoxene or evenly distributed in the two zones of leucoxene.
2003302 (East Tennessee)		0.32	Remnants of ilmenite surrounded by leucoxene in two or more zones, one P-rich, the other Fe-rich.
2003303 (Florida)		0.16	Ilmenite completely altered to leucoxene, in which P is concentrated.
2003304 (India)		0.13	Intensely altered ilmenite commonly with two zones of leucoxene. P concentrated in some leucoxene.
ILUKA-FLA 101503-93	5	0.15	Intensely altered ilmenite with rare original ilmenite remnants. P concentrated in leucoxene.
VIETNAMESE E98651-105	5-10	0.11	Weakly to strongly altered ilmenite. P is concen- trated in some leucoxene.
2003305 (Malaysia)		0.18	Intensely altered ilmenite with some original ilmenite remnants. P weakly concentrated in some leuco- xene grains.
MALAYSIAN 101303-35A	8	0.15	Several degrees of alteration. Some leucoxene shows increased P together with Al and Si.
2003306 (Ukraine)		0.12	Intensely altered ilmenite grains with two zones of leucoxene. P is occasionally weakly concentrated in the inner leucoxene zone.
AUSTRA-ILUKA E105202-19	? 8	? 0.08	Weakly altered ilmenite, with P evenly distributed in leucoxene and detrital ilmenite.
2003307 (Vietnam)		0.14	Possibly two ilmenite sources? P is evenly distributed in weakly altered ilmenite, but concentrated in leucoxene in intensely altered ilmen- ites.
AUSTRA-CSL E105202-2	8	0.08	Not analysed.
AUSTRA-TIWES TC-!OX-2001T	8	0.08	Not analysed.
ILUKA-VIRGINI 10.15.03-91	10	0.07	Several degrees of alteration. P only rarely concen- trated in leucoxene.
DORAL 10.22.08-97	10	0.03	Altered ilmenite grains with some with detrital coress. P evenly distributed in the leucoxene altered part of the grain and in the detrital ilmenite.

Quantitative analyses

The quantitative microprobe analyses have been performed on the same samples as the element mapping, with the exception of the Malaysian 101303-35A and the Iluka-Virgini 101503-93 samples, which have not been quantitatively analysed.

The comparison of remnants of original ilmenite and there alteration products in the individual grains show no relation between the original P_2O_5 content in the detrital ilmenite grains with that in its alteration product (Fig. 5). This is also documented by the fact, that generally, most samples show increasing P_2O_5 content with increasing TiO₂ content (Fig. 6). The TiO₂ content, being the main constituent of leucoxene, reflects the degree of alteration, the higher the TiO₂ content the more intense the alteration. However, samples of high Scott rank (Doral 102208-97 and Austra-Iluka E105202-19) do not follow this general trend, as they typically contain only low phosphor-us alteration products (Fig. 7).

The ilmenite alteration products in most of the samples investigated has increasing amounts of Al_2O_3 with increasing P_2O_5 content (Fig. 8 and 9). The only exceptions are the Australian samples (Doral 102287-97, Iluka-FLA 101503-93 and Austra-Iluka E105202-19), which have alteration products of low phosphorus content despite high aluminium content. Some samples (East Tennessee 2003302, Ukrainian 92203-24, Ukraine 2003306, Indian E105202-7, India 2003304) show a weak tendency of increasing SiO₂ with increasing P_2O_5 content in the alteration products (Fig. 10 and 11). On the contrary several samples have increasing CaO contents in association with increasing P_2O_5 and Al_2O_3 contents (Fig. 12 and 13). The exceptions are the Malaysian (2003304), the Vietnamese (Vietnam 2003307, E98651-105) and the Australian (Doral 102208-97 and Austra-Iluka E105202-19) samples, which all have very low CaO contents.



Figure 5. Comparable microprobe measurements in remnants of the original ilmenite and its alteration product from the same grain. Only selected samples with abundant remnants of original ilmenite cores surrounded by leucoxene alteration product have been plotted. Note there seems to be no relation between the phosphorus content in the detrital ilmenite and its alteration product.



Figure 6. Quantitative analyses of ilmenite alteration products show generally increasing P_2O_5 content with increasing TiO₂ content.



Figure 7. Quantitative analyses of ilmenite alteration products in samples of high Scott rank (Doral 102208-97 and Austra-Iluka E105202-19) show no relationship between P_2O_5 and TiO_2 contents.



Figure 8. Quantitative analyses of ilmenite alteration products show generally increasing P_2O_5 content with increasing Al_2O_3 content, with the exception of the Ilkua-FLA sample.



Figure 9. Quantitative analyses of ilmenite alteration products in samples of high Scott rank (Doral 102208-97 and Austra-Iluka E105202-19) show no relationship between P_2O_5 and Al_2O_3 contents.



Figure 10. Quantitative analyses of ilmenite alteration products in some samples show a weak tendency of increasing P_2O_5 content with increasing SiO₂ content.



Figure 11. Quantitative analyses of ilmenite alteration products in samples of high Scott rank (Doral 102208-97 and Austra-Iluka E105202-19) show no relationship between P_2O_5 and SiO₂ contents.



Figure 12. Quantitative analyses of ilmenite alteration products show generally increasing P_2O_5 content with increasing CaO content, with the exception of the Vietnamese samples which are always low in CaO content.



Figure 13. Quantitative analyses of ilmenite alteration products in samples of high Scott rank (Doral 102208-97 and Austra-Iluka E105202-19) show no relationship between P_2O_5 and CaO contents. The Ukraine 2003306 sample, though, indicate some relationship.

CCSEM

		-	0		,				
	Method			Ilmenite				Calculate	ed
				altera-		Ilmenite		P_2O_5 (wt	%) in
			Dulla	tion	T - 4 - 1	+ leuco-	Mona-	monazite	, calcu-
	Sample	0.004	Bulk	product	Total	xene	zite	lated fr	om Ce
GEUS		Scott	P_2O_5	$P_2 O_5$	$P_2 O_5$	$P_2 O_5$	$P_2 O_5$		
NO.		rank	(Wt%)	(Wt %)	(Wt %)	(Wt %)	(Wt %)	ICP-INS (
				Micro-					XRF
			XRF	probe	CCSEM	CCSEM	CCSEM	ICP-MS	DuPont
2002602	UKRAINIAN	1	0.12	0.12	0 1 2 5	0 1 1 0	0.016		0.007
2002002	92203-24	•	0.12	0.12	0.155	0.119	0.010		0.007
	DORAL								0.025
2001142	102208-97	10	0.03	0.04	0.335	0.038	0.297		+/-
	102200 37								0.02*
2001180	INDIAN	1	0 15	0.16	0 266	0 126	0 14		
2001100	E105202-7		0.10	0.10	0.200	0.120	0.11		
2002802	VIETNAMESE	7	0.11	0.17	0.155	0.073	0		0.012
	E98651-105		_	_			_		
2003302	East Tennessee		0.32	0.26	0.206	0.206	0	0.066	
2003303	Florida		0.16	0.21	0.172	0.172	0	0.003	
	Malauria								
2003305	ivialaysia		0.18	0.10	0.168	0.123	0.045	0.022	
	India								
2003304	Inula		0.13	0.12	0.222	0.123	0.099	0.018	
	Likraine								
2003306	Okraine	3	0.12	0.15	0.144	0.109	0.035	0.008	
	Vietnam								
2003307			0.14	0.11	0.313	0.099	0.023	0.007	
	AUSTRA-ILUKA	_					_		
2001178	E1005202-19	8	0.08	0.04	0.069	0.069	0		
	MALAYSIAN	-	0.45		0.470				0.040
2002102	10.13.03-35A	8	0.15		0.173	0.118	0		0.018
0004440	ILUKA-VIRGINI	40	0.07		0.000	0.000	0		
2001140	101503-91	10	0.07		0.083	0.083	0		
0001111	ILUKA-FLA	-	0.45		0.400	0.400	0		
2001141	101503-93	5	0.15		0.100	0.166	0		
2001170	AUSTRA-CSL	0	0.09		0.112	0 1 1 2	0		
2001179	E105202-2	0	0.08		0.112	0.112	U		
2003530	Australian		0 232		0.095	0.042	0.053		0.0502
2000000	BMAX ilmenite		0.20		0.000	0.042	0.000		0.000
	Australian								
2003531	BMAX leuco-		0.23?		0.259	0.134	0.125		
	xene								
2003532	Australian		0.23?		0 113	0 113	0		
2000002	BMAX rutile		0.20		0.110	0.110			

Table 3. P_2O_5 contents attained by different methods.

2003533	Brazil Imerys				0.032	0.032	0		
Monazite has been measured by CCSEM and calculated from the Ce content measured by ICP-MS and									
XRF, respectively. Note that the * indicates an average value for all Doral samples.									

As phosphorus causes problems during processing of ilmenite ore, phosphorus content measured by several different methods have been compared (Table 3). For each sample the average P_2O_5 content in ilmenite and its alteration product obtained by microprobe correlates well with the average P_2O_5 in ilmenite and leucoxene obtained by CCSEM (Table 3, Fig. 14). This is notable, as the microprobe results comprise measurements in 4 to 12 points of approximately 40 single grains per sample, whereas the CCSEM results are based on scanned areas of 1500–2000 grains per sample. The accuracy and precision of P_2O_5 measurements is substantially higher for the microprobe than the CCSEM. However, the statistical validity is much higher for CCSEM results than for the microprobe due to the larger number grains analysed by CCSEM.

The bulk XRF P_2O_5 contents show fine correlation to the P_2O_5 in ilmenite and leucoxene grains obtained by CCSEM (Fig. 15), though the CCSEM results, as expected, are a little lower than the XRF results. The total P_2O_5 content obtained by CCSEM has poor correlation to the bulk XRF P_2O_5 content (Fig. 15). Samples containing monazite and xenotime seem to be overestimated in total P_2O_5 content. Monazite and xenotime occur as 1 or 3 grains out of 1500–2000 grains, therefore the statistical accuracy is very low. The maximum amount of monazite has been calculated on the basis of the amount of Ce (assuming that all Ce is incorporated in monazite) from XRF or ICP-MS results (Table 3). The calculated monazite amount and the CCSEM measured amount of monazite also show a poor correlation, due to both inaccuracy by the CCSEM method and possibly also problems with estimation of monazite on its Ce content.

When comparing the Scott rank with the different methods for evaluating the adversely affecting P_2O_5 content (Fig. 16) CCSEM (ilm + leu) and bulk XRF seem to correspond to the Scott rank better than microprobe analyses and CCSEM (total content of phosphorus bearing minerals). Combination of CCSEM (ilmenite + leucoxene) and calculated monazite and xenotime based on bulk XRF Ce and Y, respectively, seem to correlate with the Scott rank in a similar way as CCSEM (ilm + leu). Still though there seems to be room for adjustment before the Scott rank can be estimated by an analytical method alone.







Figure 15. Comparison of P_2O_5 content obtained by XRF of bulk sample and by scanning 1500–2000 grains per sample by CCSEM. Note that the average phosphorus content of ilmenite and leucoxene by CCSEM correlates well with the bulk XRF phosphorus content, whereas the total phosphorus content by CCSEM is overestimated in some samples.



Figure 16. Comparison of Scott rank and average P_2O_5 content obtained by CCSEM (*il-menite+* leucoxene), CCSEM (total), microprobe (*ilmenite* alteration products), XRF (bulk sample) and a combination of CCSEM (*ilmenite +* leucoxene) and XRF (calculation of P_2O_5 contribution from monazite based on Ce content from XRF).

P₂O₅ in ilmenite in relation to depositional environment

The geochemical database comprises information from several ilmenite ore samples from Denmark, India and Madagascar, which gives the opportunity to compare ilmenite alteration with different depositional environments. Samples from the investigated countries show a general increase in P_2O_5 content with increasing degree of ilmenite alteration, which can be illustrated by increased amount of TiO₂ content in ilmenite; and increased P_2O_5 content with an increased amount of Ti-minerals in the heavy mineral fraction (Fig. 17–22).

India

The bedrock samples (including khondalite suite rocks, charnockitic rocks and hornblendebiotite gneiss) are characterised by low P_2O_5 contents in ilmenite (Fig. 17 and 18). On the other hand beach sand, sourced by khondalite suite rocks (Bernstein, 2003), shows a considerably higher P_2O_5 content and a dominance of strongly altered ilmenite with 58–63 wt% TiO₂ (Fig. 18). Beach sand, sourced from the Cenozoic sediments (Bernstein, 2003), and river sands are characterised by low P_2O_5 and low TiO₂ contents in ilmenite grains (Fig. 17 and 18). The Teri sand, with a possible Aeolian origin, has a medium content of P_2O_5 in ilmenite grains despite the low TiO₂ contents in ilmenite (Fig. 18). The Teri sand samples are unusual in having ilmenite grains low TiO₂ contents and at the same time having high concentration of Ti-minerals in the heavy mineral fraction.

Denmark

A considerable number of samples have been taken from Skjern-Stauning and Vorslunde, which form two distinct clusters in Fig. 19 and 20. The deposit at Vorslunde is interpreted as shoreface sands with wash-over fans in a barrier island environment (Knudsen et al., 2005b). The Vorslunde samples are characterised by high P_2O_5 and TiO₂ contents (Fig. 20). The Skjern-Stauning samples are divided into Miocene, Quaternary and unknown. The Skjern-Stauning Miocene deposits are interpreted as outer shoreface-shallow marine (Rasmussen, 2004; Rasmussen et al., 2004; Knudsen et al., 2005a). The Skjern-Stauning Quaternary deposits have very low P_2O_5 (< 0.05 wt%) and low TiO₂ contents. The Skjern-Stauning Miocene deposits are characterised by low-medium P_2O_5 content (0.05-0.10 wt%) and low in TiO₂ content (Fig. 20). The recent marine deposits from Vestkysten, Jyske Rev and Horns Rev all group together close to the other shallow marine Miocene deposits at Skjern-Stauning (Fig. 20). Other Miocene deposits (Vemb, Sønder Omme, Videbæk, Møborg, Filskov Mark, Hastrup) all have high P_2O_5 content (0.10–0.20 wt%) and varying TiO₂ content (Fig. 20). Several Miocene marine deposited samples (Skjern-Stauning and Kibæk) have high contents of Ti-minerals, which generally have low amounts of TiO₂ and P₂O₅. This particular trend is similar to the Teri sand from India.



Figure 17. Graph showing the total amount of Ti-minerals (ilmenite, leucoxene, titanomagnetite and rutile) in the heavy minerals fraction obtained by CCSEM plotted against the average P_2O_5 content in ilmenite and its alteration products also from CCSEM.



Figure 18. Graph showing TiO_2 content in ilmenite grains obtained by CCSEM plotted against the average P_2O_5 content in ilmenite and its alteration products also from CCSEM.



Figure 19. Graph showing the total amount of Ti-minerals (ilmenite, leucoxene, titanmagnetite and rutile) in the heavy minerals fraction obtained by CCSEM plotted against the average P_2O_5 content in ilmenite and its alteration products also from CCSEM.



Figure 20. Graph showing the TiO_2 content in ilmenite grains obtained by CCSEM plotted against the average P_2O_5 content in ilmenite and its alteration products also from CCSEM.

Madagascar

The highest P_2O_5 content (0.10–0.15 wt%) is found in ilmenite grains with high TiO₂ content and comes from active dunes in an area dominated by cordierite schist, i.e. Khondalite suite rocks (Bernstein, 2004) in the western part of southern Madagascar (Fig. 21 and 22). All other samples with P_2O_5 content > 0.10 wt% are also from this area, despite the depositional environment being river, stabilised dune or weathering product of bedrocks. The active dunes in the southern part of southern Madagascar with Phanerozoic cover (Bernstein, 2004) have much lower P_2O_5 content (0.05–0.07 wt%) and active dunes in the western part of southern Madagascar also with Phanerozoic cover have the lowest P_2O_5 content (0.003–0.04 wt%) of all. The ilmenite grains from these active dunes generally have a low TiO₂ content of 52–55 wt%. Beach sediments have ilmenite grains with P_2O_5 contents of 0.04–0.07 wt% and varying TiO₂ content (Fig. 22). The ilmenite grains from river deposits generally seem to be similar to beach sediments with low ilmenite P_2O_5 contents (0.03–0.06 wt%) and varying TiO₂ contents. Ilmenite grains from flat sand plains show a larger variation in the P_2O_5 content (0.01–0.09 wt%) and also a varying TiO₂ content (Fig. 22). Borehole samples from the Phelps Dodge ore zone have ilmenite grains characterised by low P_2O_5 content (< 0.08 wt%) and low TiO₂ content (51–53 wt%).



Figure 21. Graph showing the total amount of Ti-minerals (ilmenite, leucoxene, titanomagnetite and rutile) in the heavy minerals fraction obtained by CCSEM plotted against the average P_2O_5 content in ilmenite and its alteration products also from CCSEM.



Figure 22. Graph showing TiO_2 content in ilmenite grains obtained by CCSEM plotted against the average P_2O_5 content in ilmenite and its alteration products also from CCSEM.

Discussion

Location of phosphorus in ilmenite

All results clearly suggest that P_2O_5 enters the alteration product of ilmenite. The element mapping shows a strong relation between altered parts of the ilmenite grains and relative increase in TiO₂ and P_2O_5 contents (Fig. 2 and 3, Appendix 1). The quantitative analyses show that the phosphorus content in the detrital ilmenite grains has no influence on the phosphorus content in the alteration products (Fig. 5) and that P_2O_5 generally increases with increasing TiO₂ content (Fig.6). Furthermore, samples of presumably similar source areas – East Tennessee and Florida (Roger McLimans, personal communication) show different types of alteration. Therefore the transport and the depositional environment can be decisive for the alteration and the incorporation of phosphorus.

Selected element maps also indicate that Al_2O_3 and SiO_2 , and occasionally CaO, seem to be related to alteration of ilmenite and relatively increased TiO_2 and P_2O_5 contents. Some ilmenite grains have several alteration zones with alternating compositions from high TiO_2 and P_2O_5 contents to high Fe_2O_3 content (Fig. 1 and 3). Several zones in the altered ilmenite grains suggest alternating pore fluid compositions or changing depositional environment.

Alteration of ilmenite

The alteration of ilmenite ($Fe^{2+}TiO_3$) takes place through two steps: pseudorutile and leucoxene. Pseudorutile, the first intermediary alteration product of ilmenite, has the chemical composition $Fe^{3+}_2O_3 \cdot nTiO_2 \cdot mH_2O$ (3 < n < 5, 1 < m < 2) (Temple, 1966; Grey & Reid, 1975). The alteration products of ilmenite with the chemical composition of pseudorutile have been identified in all samples. However, as the samples have not been investigated by XRD or reflection microscopy the presence of pseudorutile cannot be verified. Formula considerations indicate that ilmenite loses Fe and that the remaining iron is oxidised during its first alteration. According to Temple (1966) the crystal structure changes from trigonal in ilmenite to a primitive hexagonal crystal structure in pseudorutile. The mechanism of pseudorutile formation presumably involves the loss of iron by diffusion trough the lattice and oxidation of the remaining iron (Grey & Reid 1975; Dimanche & Bartholomé 1976). Manganese and magnesium are common constituent in detrital ilmenite. Manganese seems to remain in the first alteration product of ilmenite, presumably pseudorutile (Fig. 1 and 3, Appendix 1).

Leucoxene, the final alteration product of ilmenite, mainly consists of small TiO₂ crystals. Various degrees of alteration of ilmenite to leucoxene have been observed in all investigated samples. The transformation of pseudorutile into leucoxene requires a complete rear-

rangement of the crystal structure (from hexagonal to tetragonal or orthorhombic), since both iron and oxygen must be removed. Incongruent dissolution seems the most likely way of forming leucoxene from pseudorutile (Dimanche & Bartolemé 1976; Weibel 2003). Thereby pseudorutile is stepwise dissolved and TiO_2 is epitactic (i.e. crystal orientation similar to the substrate on which it grew) precipitated in a porous network. Fe and Mn remains in solution or are incorporated into other minerals.

Alteration products with strong zonation occur in some altered ilmenite grains (Fig. 1 and 3). Some of these zones are iron enriched and some P-enriched (Fig. 1 and 3, Appendix 1). Fe-rich zones, next to detrital ilmenite, are probably caused by the alteration product – pseudorutile. However, Fe-rich zones may also occur as the outermost rim (Appendix 1) and is then most likely due to secondary impregnation of the leucoxene network by iron oxide/hydroxide needles, as previously described by Weibel & Friis (2004). In a similar way it can be expected that other minerals can precipitate inside the porous leucoxene network.

The element mapping of selected grains has shown that P-rich zones typically are associated with relatively higher amounts of Al_2O_3 and commonly higher CaO contents. Furthermore quantitatively analyses of altered ilmenite show a correlation between P_2O_5 and Al_2O_3 and (CaO) in most samples (Fig. 8, 12 and 13). A possible explanation could be incorporation of minute aluminium phosphate minerals in the porous leucoxene network. Aluminium phosphate and aluminium phosphate sulphate minerals are commonly, but only rarely identified early diagenetic minerals in fluviatile and shallow marine environment (Rasmussen et al. 1998; Pe-Piper & Dolansky 2005; Gall & Donaldson, 2006). The minerals of interest could be crandallite group minerals, which are similar to $CaAl_3(PO_4)_2(OH)_5 \cdot (H_2O)$, but with substitution of Ca by REE and other elements. Deviation from the trend in Fig. 12 and 13 could be caused by varying amount of REE and other elements substituting for CaO.

When phosphorus and iron occur as alternating zones (Fig. 1), it may indicate fluctuating availability of P and Fe in the pore fluid during ilmenite alteration, or it may be the result of varying geochemical conditions. Incorporation can take place gradually during ilmenite alteration or afterwards reflecting the surrounding geochemical environment.

Depositional environment influence on the P₂O₅ content

The Indian Beach sand and the Madagascar active dunes, both sourced by khondalite suite rocks (Bernstein, 2003; 2004) are characterised by ilmenite with relatively high P_2O_5 contents, even though Indian khondalite samples show only low P_2O_5 contents in ilmenite (Bernstein, 2003). The coast parallel sand bars and coastal dunes in India have been strongly modified by human activity (Bernstein, 2003). The beach samples from India might therefore be comparable with beach and dune samples from Madagascar. For southern Madagascar and southern India there seem to be a coincidence between humid tropical climate and the occurrence of highly altered ilmenite with the highest P_2O_5 content. Consequently, the coincidence of khondalite suite rocks as source rock and a humid tropical climate results in intensive alteration of ilmenite and incorporation of high amounts of phos-

phorus in both beach and Aeolian depositional environments. Khondalite suite rocks may have liberated P_2O_5 from other phosphorous minerals; or phosphorus could have been liberated during degradation of organic material in the wet tropical climate. Authigenic aluminum phosphate minerals and alumino phosphate sulphate minerals have been described from an environment of intensive weathering (Pe-Piper & Dolansky 2005). Intensive weathering lead to increased availability of phosphorus and intensified ilmenite alteration, which promotes the incorporation of phosphorus minerals into the porous structure of altered ilmenite.

In the more arid parts of Madagascar (western and southern south Madagascar) the alteration is less pronounced, and therefore the phosphorus content is smaller in both river deposits and dune sand. Indian river deposits also show low degrees of alteration, though it appears to increase downstream. The Quaternary Danish deposits contain ilmenite grains with very low P_2O_5 (< 0.05 wt%) and low TiO₂ contents. Quaternary glacial deposits have been exposed to the shortest and least intensive alteration in the arctic and later temperate climate. The Quaternary material could contain reworked local Miocene deposits; however the low TiO₂ and P_2O_5 content indicate that the amount of strongly altered reworked material is low. Depositional environments, characterised by low degree of weathering either due to dry or cold climate or relatively young age, seem to be dominated by ilmenite with low P_2O_5 (< 0.05 %) and relatively low TiO₂ content.

The difference in ilmenite alteration between the Skjern–Stauning Miocene deposits (ilmenite low in TiO₂ and P₂O₅) and the Miocene Voerslunde deposits with ilmenite characterised by higher TiO₂ and P₂O₅ contents probably resulted from intensified alteration taking place in the shoreface and barrier environment compared to the outer shoreface. The Miocene in Denmark was characterised by a warm temperate to subtropical climate (Friis, 1979), and the alteration of heavy minerals has been enhanced during these conditions especially where leaching effects were largest.

In Denmark ilmenite grains with the lowest P_2O_5 content and relatively high TiO₂ content is found in some of the Jurassic–Cretaceous Bornholm samples. Preliminary investigation of continental deposits from Addit in Denmark and Poland suggest that a continental environment may promote ilmenite alteration with high TiO₂ and low P_2O_5 contents. This is of special interest and needs further investigations.

Evaluation of ore quality

Scott rank is a purely empirical evaluation of the ilmenite ore quality based on the behaviour during production (Roger McLimans, personal communication, 2006). Consequently, the aim is to find a measurable method to predict the Scott rank, i.e. the ore quality. Several methods: bulk XRF, CCSEM, microprobe analysis and combinations of these has been evaluated in this investigation. The bulk XRF analysis routinely performed by DuPont gives the total P_2O_5 content. With a bulk P_2O_5 content below 0.1 wt% there has not been observed any problems during production. With a bulk P_2O_5 content above 0.1 wt% the ore might perform well or very badly. If phosphorus is situated in monazite or xenotime it will not cause as many problems as phosphorus situated in illmenite and leucoxene (Dirk Frei, personal communication, 2006).

CCSEM investigations have lead to a new determination of the ore quality – the RFTiPNo. The RFTiPNo. is the fraction of P_2O_5 located in ilmenite + leucoxene divided by the total amount of P_2O_5 also obtained by the CCSEM analyses. Ranking by the RFTiPNo. is almost similar to the ranking given from the Scott rank, but there is room for improvement. As seen in Fig. 15 and 16 the total P_2O_5 content based on CCSEM seems less reliable than the P_2O_5 content in ilmenite + leucoxene, especially when monazite or xenotime are found in the samples. This is due to occasional overestimation of these particular minerals due to their statistically low occurrence. Therefore application of the Ore quality. Estimation of the amount of monazite might be more correct when calculated from the XRF–measured Ce content.

Conclusion

Several investigations support the presence of phosphorus in the alteration products of ilmenite grains. The element maps of selected ilmenite ore samples show a relative increase in the P_2O_5 content in the altered parts of ilmenite, where the TiO_2 content is also higher. Microprobe analysis of selected ilmenite ore samples shows increased P_2O_5 content with increasing TiO_2 (i.e. increased degree of alteration of ilmenite), Al_2O_3 and partly CaO contents and rarely with increasing SiO_2 . contents. The CCSEM studies of all ore samples to date from Denmark, India and Madagascar show increased P_2O_5 content with increasing TiO_2 content in ilmenite.

The alteration of ilmenite takes place through two steps: pseudorutile and leucoxene. Pseudorutile forms by iron diffusion through the ilmenite lattice and oxidation of the remaining iron. Leucoxene forms by a complete rearrangement of the crystal structure and presumably takes place by an incongruent dissolution process followed by epitactic precipitation in a porous network. The evidence from both element maps and microprobe investigations show a coincidence between increased P_2O_5 content and increased Al_2O_3 and partly CaO and SiO₂ contents. This could be accounted for by the presence of minute alumino phosphates and/or alumino phosphate sulphates, which may have formed in the porous network of leucoxene in the altered parts of ilmenite.

Even though the alteration of ilmenite begins in the bedrock, phosphorus is not introduced in substantial amounts at this stage. Possibly more intensive alteration of the surrounding rocks and/or organic matter is necessary in order to liberate phosphorus, before phosphorus minerals can form in the porous network of the altered ilmenite grains.

In the wet tropical climate of India and Madagascar intensive alteration of Khondalite suite rocks has resulted in beach and dune deposits with locally high P_2O_5 contents in strongly altered ilmenite grains (Fig. 18 and 22). The Danish Miocene shoreface deposits with wash-over fans on barrier islands (Vorslunde in Fig. 19 and 20) show as high (or even higher) degree of ilmenite alteration and associated phosphorus incorporation as the recent samples from a wet tropical climate. The Miocene of Denmark was characterised by a warm temperate to subtropical climate and consequently the alteration started under similar climatic conditions and continued presumably at a slower rate until to day. The Miocene shallow marine deposits (Skjern-Stauning in Fig. 19 and 20) show less alteration and less phosphorus incorporation than the contemporaneous Vorslunde samples. This indicates that the depositional environment, and maybe the possibility of leaching, influences the degree of alteration as the climatic conditions must have been similar. The river deposits and the marine sand from India and Madagascar, and the Quaternary glacial deposits from Denmark contain the least altered ilmenite grains which thus have the lowest P_2O_5 content (Fig. 18, 20 and 22). Young sediments (river deposits), sediments characterised by a low degree of leaching (shallow marine sediments) and sediments from an arctic to temperate climate (Quaternary glacial deposits) show a low degree of alteration in ilmenite and presumably also a source with limited amounts of phosphorus.

Previously the Scott rank has been estimated by the RFTiPNo. (representing the fraction of P_2O_5 located in ilmenite + leucoxene divided by the total amount of P_2O_5 , both obtained by

CCSEM analyses). However, the total amount of P_2O_5 from CCSEM is subject to a larger uncertainty than the P_2O_5 content from CCSEM (ilmenite + leucoxene). The estimation of the amount of monazite and xenotime, based on the bulk XRF content of Ce, do not give a substantially improved total of P_2O_5 content. The application of the P_2O_5 content for CCSEM ilmenite + leucoxene might give an improved prediction of the ore quality. Briefly the evaluation of ore quality can be done in the following way:

XRF bulk rock: $P_2O_5 < 0.1$ %	NO PROBLEMS EXPECTED
XRF bulk rock: $P_2O_5 > 0.1$ %	CCSEM DETAILED TEST REQUIRED
CCSEM ilmenite + leucoxene: $P_2O_5 < 0.1 \%$	ON BASIS OF TI-MINERAL COMPOSITION NO PROBLEMS EXPECTED
CCSEM ilmenite + leucoxene: $P_2O_5 = 0.1$ %	BORDERLINE PRECAUTION TO POSSIBLE PROBLEMS
CCSEM ilmenite + leucoxene: $P_2O_5 > 0.1$ %	PROBLEMATIC RESPONSE EXPECTED

Recommendations

- Continued CCSEM analyses of continental deposits in order to confirm the preliminary results of ilmenite characterised by high TiO₂ and low P₂O₅ from continental deposits.
- Continuation of investigation of impurities incorporated into ilmenite during its alteration. Are other elements, such as AI, Si, Mg, S, incorporated simultaneously with phosphorus in all environments?
- Compilation of ilmenite ore XRD (X-ray diffraction) analysis in order to test a hypothesis of phosphorus having difficulty entering the pseudorutile lattice, whereas it has easy access to the porous network of leucoxene. Pseudorutile-dominated ores might then be the best ore type.

Acknowledgement

Roger McLImans, Christian Knudsen, Dirk Frei and Stefan Bernstein are thanked for constructive comments and Stuart Watt is thanked for correcting the English languish.

References

- Bernstein, S. 2003: Ilmenite heavy sand deposits, South India provenance and chemistry clues to their origin. Danmarks og Grønlands Geologiske Undersøgelse Rapport **2003/100**, 123p.
- Bernstein, S. 2004: Heavy sand deposits in southern Mdagascar. Results of a CCSEM study of coastal sediments, with particular emphasis on compositional distribution of ilmenite and garnet. Danmarks og Grønlands Geologiske Undersøgelse Rapport **2004/11**, 38p.
- Dimanche, F. & Batholomé, P. 1976: The alteration of ilmenite in sediments. Minerals, Science and Engineering **8**, (3) 187–201.
- Friis, E. M. 1979: The Damgaard flora: A new Middle Miocene flora from Denmark. Bulletin of Geological Society of Denmark **27**, 117–142.
- Gall, Q. & Donaldson, J. A. 2006: Diagenetic fluorapatite and aluminium phosphatesulphate in the Paleoprotorozoic Thelon Formation and Hornby Bay Group, northwestern Canadian Shield. Canadian Journal of Earth Science **43**, 617–629.
- Grey, I. E. & Reid, A. F. 1975: The structure of pseudorutile and its role in the natural alteration of ilmenite. American Mineralogist **60**, 898–906.
- Knudsen, C., Frei, D. Rasmussen, T. Rasmussen, E. S. & McLimans, R. 2005a: New methods in provenance studies based on heavy minerals: an example from Miocene sands in Jylland, Denmark. In: Sønderholm, M. & Higgins, A. K. (Eds.) Review of Survey activities 2004. Geological Survey of Denmark and Greenland Bulletin 7, 29–32.
- Knudsen, C., Rasmussen, T., McLimans, R., Jørgensen, T. G., Fischer, T. & Frei, D.
 2005b: Multi method approach to heavy mineral exploration: Miocene of Denmark.
 Heavy Minerals 2005, Society for Mining, Metallurgy, and Exploration, 83–90.
- Pe-Piper, G. & Dolansky, L. M 2005: Early diagentic origin of Al phosphate-sulfate minerals (woodhouseite and crandallite series). American Mineralogist **90**, 1434–1441.
- Rasmussen, B. Buick, R. & Taylor, W. R. 1998: Removal of oceanic REE by authigenic precipitation of phosphatic minerals. Earth and Planetary Science Letters 164, 135– 149.
- Rasmussen, E. S. 2004: Stratigraphy and depositional evolution of the uppermost Oligocene-Miocene succession in western Denmark. Bulletin of the Geological Society of Denmark **51**, 89–109.
- Rasmussen, E. S., Dybkjær, K. & Piasecki, S. 2004: The Billund delta: a possible new giant aquifer in central Jutland. Geological Survey of Denmark and Greenland Bulletin 4, 21–24.
- Stendal, H. 2004: Heavy mineral sands in Vietnam 2003. Danmarks og Grønlands Geologiske Undersøgelse Rapport **2004/31**, 31p.
- Temple, A. K. 1966: Alteration of ilmenite. Economic Geology 61, 695–714.
- Weibel, R. 1998: Diagenesis in oxidising and locally reducing conditions an example from the Triassic Skagerrak Formation, Denmark. Sedimentary Geology **121**, 259–276.
- Weibel, R. 2003: Alteration of detrital Fe-Ti oxides in Miocene fluvial deposits, central Jutland, Denmark. Geological Society of Denmark **50**, 171–183.

Weibel, R. & Friis, H, 2004: Opaque minerals as keys for distinguishing oxidising and reducing diagenetic conditions in the Lower Triassic Bunter Sandstone, North German Basin. Sedimentary Geology 169, 129–149.

Appendix 1

Element maps

Indian E105202-7



Ilmenite remnants (white BSC) appear in a box-work texture surrounded by two generations of leucoxene. Phosphorus is con-centrated in the outermost leucoxene type (dark grey BSC), the innermost leucoxene type (light grey BSC) and the ilmenite remnants (white BSC) have low content of P. Black box on BSC shows the mapped area.

	Leucox.	"Ilmenite"
143	(average)	(average)
AI_2O_3	1.31	0.33
MnO	1.05	1.63
TiO ₂	62.43	58.71
P_2O_5	0.19	0.03
Na ₂ O	0.07	0.02
SiO ₂	0.15	0.07
FeO	29.08	33.57
CaO	0.05	0.02
MgO	1.03	1.24
Total	95.47	95.70



Indian E105202-7



Phosphorus is concentrated in the leucoxene (dark grey BSC) altered part, whereas ilmenite remnants (white BSC) have low content of P. Black box on BSC shows the mapped area.

	Leucox.	"Ilmenite"
148	(average)	(average)
Al ₂ O ₃	2.36	1.15
MnO	0.68	2.04
TiO ₂	70.19	62.89
P_2O_5	0.47	0.26
Na ₂ O	0.10	0.15
SiO ₂	0.20	0.17
FeO	21.25	29.24
CaO	0.19	0.12
MgO	0.51	0.78
Total	95.99	96.92



Ukrainian 9.22.03-94



Phosphorus is distributed in equal amounts in the slightly altered detrital ilmenite (light grey) and leucoxene altered parts (dark grey). Remnants of ilmenite (white) though have relatively low P content. Black box on BSC shows the mapped area.



Ukrainian 9.22.03-94



Element map 136 (060606)	
Scott rank:	1 (very bad)
CCSEM P2O5 ilm + leu:	0.13 wt%

Phosphorus appears in higher concentrations in the leucoxene altered parts of the grain (dark grey) than in the least altered parts (light grey). Black box on BSC shows the mapped area.



2003302 (East Tennessee)



Element map 27 (060606) CCSEM P₂O₅ ilm + leu: 0.21 wt%

Phosphorus is concentrated in leucoxene altered parts (dark grey) whereas detrital ilmenite remnants (light grey, for example in top of black box) have low P content. The second alteration zone around the outermost rim and along fissures (light grey, for example in the lower right corner of the black box) is Ferich and has a relatively low P content. This could be due to two-stage alteration, first leucoxene formation and secondly impregnation of the porous leucoxene mesh with iron-oxide/ hydroxide needles (Weibel, 1998). Black box on BSC shows the mapped area.

Leucox.	Ilmenite
(average)	(average)
1.18	0.46
0.14	1.30
69.04	59.80
0.46	0.11
0.10	0.05
0.53	0.19
22.02	31.63
0.16	0.06
0.09	0.24
93.71	93.84
	Leucox. (average) 1.18 0.14 69.04 0.46 0.10 0.53 22.02 0.16 0.09 93.71



2003302 (East Tennessee)



Element map 16 (060606) CCSEM P_2O_5 ilm + leu: 0.21 wt%

Phosphorus is concentrated in the outermost leucoxene altered zone (darkest grey) whereas the innermost leucoxene zone (medium grey) and the original ilmenite remnants (white) have low P content. Black box on BSC shows the mapped area.

	Leucox.	Ilmenite
16	(average)	(average)
AI_2O_3	0.48	0.33
MnO	0.76	1.12
TiO ₂	66.96	62.12
P_2O_5	0.13	0.06
Na ₂ O	0.06	0.03
SiO ₂	0.32	0.21
FeO	24.31	29.78
CaO	0.15	0.07
MgO	0.08	0.09
Total	93.25	93.79



2003303 (Florida)



Element map 44 (060606) CCSEM P₂O₅ ilm + leu: 0.17 wt%

Phosphorus is concentrated in the strongest altered areas (dark grey – leucoxene 2), which resembles a honey comb texture with voids in the centre. The voids may have formed after dissolution of hematite exsolution lamellae. The least altered parts of the ilmenite (light grey – leucoxene 1) have lower P content. Black box on BSC shows the mapped area.

	Leuco. 1		Leu	со. 2
	Ligth	n grey	Dar	k grey
	in	BSC	in	BSC
44	(ave	rage)	(ave	erage)
AI_2O_3		0.47		0.61
MnO		5.53		5.31
TiO ₂		60.46		61.94
P ₂ O ₅		0.09		0.12
Na ₂ O		0.04		0.07
SiO ₂		0.09		0.08
FeO		29.25		27.27
CaO		0.01		0.02
MgO		0.03		0.04
Total		96.11		95.58



2003303 (Florida)



Phosphorus is concentrated in the most titanium-rich leucoxene areas (dark grey), whereas the least altered parts of the ilmenite (light grey) have low P content. Black box on BSC shows the mapped area.

	Leucox.	"Ilmenite"
29	(average)	(average)
AI_2O_3	1.63	0.76
MnO	0.24	0.40
TiO ₂	76.72	67.35
P_2O_5	0.36	0.16
Na ₂ O	0.03	0.02
SiO ₂	0.17	0.07
FeO	17.84	26.58
CaO	0.02	0.02
MgO	0.04	0.13
Total	0.00	0.00



2003304 India)



Element map 86 (060606) CCSEM P₂O₅ ilm + leu:: 0.12 wt%

Phosphorus is concentrated in two of the colloidal leucoxene zones, the outermost (dark grey, marked 1) and the innermost (dark grey, marked 3). A leucoxene zone, low in P and high in Fe (light grey, marked 2), occurs between these P-rich leucoxene zones. The centre of the grain consists of Fe-rich leucoxene, with a chemical composition similar to leucoxene in zone 2. Black box on BSC shows the mapped area.

86	Leuco. 1	Leuco. 2
	Dark in	Light in
	BSC	BSC
	(average)	(average)
AI_2O_3	0.73	0.12
MnO	0.84	0.84
TiO ₂	64.11	55.75
P_2O_5	0.19	0.04
Na ₂ O	0.08	0.04
SiO ₂	0.21	0.05
FeO	24.16	37.03
CaO	0.11	0.01
MgO	0.28	0.22
Total	90.70	94.10



2003304 (India)



Phosphorus is concentrated in the most titanium-rich leucoxene areas (dark grey), whereas the least altered parts of the ilmenite (light grey) have low P content. Black box on BSC shows the mapped area.

	Leucox.	Ilmenite
101	(average)	(average)
AI_2O_3	0.38	0.03
MnO	0.13	0.14
TiO ₂	63.85	53.89
P ₂ O ₅	0.12	0.02
Na ₂ O	0.07	0.01
SiO ₂	0.22	0.02
FeO	27.71	44.98
CaO	0.09	0.00
MgO	1.10	1.23
Total	93.67	100.34



Iluka-FLA 10.15.03-93



The phosphorus content seems to be reduced in remnants of the original ilmenite. The highest P content appears in cracks and could be artificially be due to increased background or be related to the polished block preparation. White box on BSC shows the mapped area.

	Leucox.	Ilmenite
7	(average)	(average)
AI_2O_3	0.60	0.24
MnO	2.63	3.75
TiO ₂	66.29	57.87
P_2O_5	0.11	0.05
Na ₂ O	0.18	0.07
SiO ₂	0.10	0.06
FeO	26.10	37.74
CaO	0.05	0.01
MgO	0.03	0.03
Total	96.09	99.82



Iluka-FLA 10.15.03-93



 $\begin{array}{ll} \mbox{Element map 10 (130606)} \\ \mbox{Scott rank:} & 5 \\ \mbox{CCSEM P_2O_5 ilm + leu:} & 0.17 \mbox{wt\%} \end{array}$

The phosphorus content seems to be reduced in remnants of the detrital ilmenite (light grey). The highest P content appears in leucoxene along cracks and might be P incorporated in leucoxene or due to epoxy impregnation in cracks. Black box on BSC shows the mapped area.

	Leucox.	Ilmenite
10	(average)	(average)
AI_2O_3	0.55	0.13
MnO	1.42	1.30
TiO ₂	64.95	57.12
P ₂ O ₅	0.23	0.04
Na ₂ O	0.11	0.02
SiO ₂	0.06	0.03
FeO	26.96	35.02
CaO	0.06	0.00
MgO	0.16	0.28
Total	94.49	93.93



Vietnamese E98651-105



 $\begin{array}{ll} \mbox{Element map 11 (050906)} \\ \mbox{Scott rank:} & 5-10 \\ \mbox{CCSEM P_2O_5 ilm + leu:} & 0.07 \mbox{wt\%} \\ \end{array}$

The phosphorus content is higher in leucoxene altered areas whereas ilmenite with intergrown rutile has lower phosphorus content. Black box on BSC shows the mapped area.

	Ilmenite	Leucox.
11	(average)	(average)
AI_2O_3	0.20	5.22
MnO	2.56	0.26
TiO ₂	54.24	78.32
P_2O_5	0.02	1.20
Na ₂ O	0.03	0.02
SiO ₂	0.18	0.61
FeO	40.05	8.04
CaO	0.00	0.01
MgO	0.06	0.03
Total	97.40	93.83



Vietnamese E98651-105



 $\begin{array}{l} \mbox{Element map 17 (050906)} \\ \mbox{Scott rank:} & 5-10 \\ \mbox{CCSEM P_2O_5 ilm + leu:} & 0.07 \mbox{wt\%} \end{array}$

The phosphorus content seems to be increased in leucoxene altered spots (dark grey) of the detrital ilmenite (light grey). Black box on BSC shows the mapped area.



2003305 (Malaysia)



Element map 113 (060606) CCSEM P₂O₅ ilm + leu: 0.12wt%

Phosphorus is concentrated in the most leucoxene altered areas (dark grey), whereas the least altered parts of the ilmenite (light grey) have low P content. Black box on BSC shows the mapped area.

	Leucox.	
	(aver-	Ilmenite
113	age)	(average)
AI_2O_3	0.51	0.02
MnO	1.66	3.44
TiO ₂	68.62	53.88
P_2O_5	0.14	0.01
Na ₂ O	0.02	0.01
SiO ₂	0.22	0.02
FeO	23.36	43.34
CaO	0.03	0.00
MgO	0.02	0.06
Total	94.59	100.76



2003305 (Malaysia)



 $Element map 117 (060606) \\ CCSEM P_2O_5 ilm + leu: 0.12wt\%$

Phosphorus is concentrated in leucoxene altered areas (dark grey) around the rim and along cracks or former exsolution lamellae. The least altered parts of the ilmenite (light grey) have low P content. Black box on BSC shows the mapped area.



Malaysian 10.13.03-35A



 Element map 29 (050906)

 Scott rank:
 8

 CCSEM P2O5 ilm + leu:
 0.12wt%

Phosphorus follows leucoxene and occurs in increased amounts in the most altered parts (dark grey) of the grain (light grey). Black box on BSC shows the mapped area.



Malaysian 10.13.03-35A



 $\begin{array}{l} \mbox{Element map 20 (130606)} \\ \mbox{Scott rank:} & 8 \\ \mbox{CCSEM P_2O_5 ilm + leu:} & 0.12 \mbox{wt\%} \end{array}$

Phosphorus occurs in highest amounts in most leucoxene altered parts (darkest grey) of the detrital ilmenite (light grey). Zones with starting leucoxene alteration (medium grey) do not seem to have increased phosphorus content. Black box on BSC shows the mapped area.



2003306 (Ukraine)



Phosphorus appears only very weakly concentrated in the innermost leucoxene alteration (dark grey), whereas the outermost Fe-impregnated leucoxene (light grey) has a slight lower P content. Black box on BSC shows the mapped area.

	Leuco. 1	Leuco. 2
	Light grey	Dark grey
	in BSC	in BSC
70	(average)	(average)
AI_2O_3	0.34	0.31
MnO	0.41	0.72
TiO ₂	66.66	66.12
P_2O_5	0.12	0.12
Na ₂ O	0.01	0.01
SiO ₂	0.33	0.32
FeO	26.00	25.23
CaO	0.07	0.09
MgO	0.43	0.50
Total	94.42	93.51



2003306 (Ukraine)



Phosphorus appears only very weakly concentrated in the most TiO_2 rich leucoxene alteration (dark grey, marked 1) compared to the leucoxene with smaller TiO_2 content (light grey, marked 2). Black box on BSC shows the mapped area.



Austra-Iluka E105202-19



 Element map 14 (130606)

 Scott rank:
 8

 CCSEM P2O5 ilm + leu:
 0.07wt%

Phosphorus is distributed in equal amounts in the detrital ilmenite remnants (light grey) and leucoxene altered parts (dark grey). White box on BSC shows the mapped area.

	Leucox.	Ilmenite
14	(average)	(average)
AI_2O_3	0.72	0.50
MnO	0.06	0.31
TiO ₂	73.36	65.75
P_2O_5	0.29	0.11
Na ₂ O	0.09	0.07
SiO ₂	0.47	0.22
FeO	18.68	27.33
CaO	0.14	0.07
MgO	0.07	0.12
Total	93.88	94.48



Austra-Iluka E105202-19



 Element map 20 (130606)

 Scott rank:
 8

 CCSEM P2O5 ilm + leu:
 0.07wt%

Phosphorus is distributed in equal amounts in the detrital ilmenite remnants (light grey) and zones of leucoxene alteration (dark grey). Black box on BSC shows the mapped area.



2003307 (Vietnam)



 $Element map 59 (060606) \\ CCSEM P_2O_5 ilm + leu: 0.10wt\%$

Phosphorus is weakly concentrated in the outermost leucoxene alteration (dark grey, marked 1), whereas the innermost leucoxene (light grey, marked 2) has a slightly lower P content. Black box on BSC shows the mapped area.

	Leuco. 1	Leuco. 2
	Dark	Light grey
	grey BSC	BSC
59	(average)	(average)
AI_2O_3	2.26	0.80
MnO	2.64	3.24
TiO ₂	61.33	56.51
P_2O_5	0.51	0.16
Na ₂ O	0.04	0.02
SiO ₂	0.07	0.04
FeO	27.03	32.92
CaO	0.03	0.00
MgO	0.08	0.08
Total	93.99	93.76



2003307 (Vietnam)



Element map 64 (060606) CCSEM P₂O₅ ilm + leu: 0.10wt%

Phosphorus appears in similar amounts in unaltered ilmenite (light grey) and in leucoxene (dark grey). Black box on BSC shows the mapped area.



Iluka-Virgini 10.15.03-91



Phosphorus occurs in increased amounts in the leucoxene altered parts (dark grey) along the outer rim and along fissures. Detrital ilmenite (light grey) seems to have a very low content of phosphorus. Black box on BSC shows the mapped area.



Iluka-Virgini 10.15.03-91



 Element map 57 (050906)

 Scott rank:
 10 (very good)

 CCSEM P2O5 ilm + leu:
 0.08wt%

Phosphorus is distributed in almost equal amounts in the detrital ilmenite (light grey) and leucoxene altered parts (dark grey) in the outer rim and along fissures. Black box on BSC shows the mapped area.





 $\begin{array}{ll} \mbox{Element map 22 (130606)} \\ \mbox{Scott rank:} & 10 \\ \mbox{CCSEM P_2O_5 ilm + leu:} & 0.04 \mbox{wt\%} \end{array}$

Phosphorus is distributed in equal amounts in the detrital ilmenite (light grey) and leucoxene altered parts (dark grey) in the outer rim and along fissures. White box on BSC shows the mapped area.

	Leucox.	Ilmenite
22	(average)	(average)
AI_2O_3	2.72	0.04
MnO	0.22	2.20
TiO ₂	73.63	53.03
P_2O_5	0.01	0.00
Na ₂ O	0.02	0.03
SiO ₂	0.37	0.01
FeO	10.84	43.38
CaO	0.01	0.00
MgO	0.03	0.05
Total	87.99	98.84



DORAL 10.22.08-97



 Element map 24 (130606)

 Scott rank:
 10

 CCSEM P2O5 ilm + leu:
 0.04wt%

Phosphorus is distributed in equal amounts in the detrital ilmenite (light grey) and leucoxene altered parts (dark grey) in the outer rim and along fissures. White box on BSC shows the mapped area.

	Leucox.	Ilmenite
24	(average)	(average)
AI_2O_3	3.30	0.01
MnO	0.21	2.48
TiO ₂	76.15	54.97
P_2O_5	0.05	0.00
Na ₂ O	0.04	0.01
SiO ₂	0.93	0.02
FeO	9.15	41.67
CaO	0.05	0.00
MgO	0.03	0.05
Total	90.00	99.31

